KINETICS OF SOLID-GAS REACTIONS IN FLUID BEDS

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JAMES DeHAVEN BATCHELOR

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KINETICS OF SOLID-GAS REACTIONS IN FLUID BEDS

Introduction

In recent years fluidization has become an important method of processing in the chemical industry. In spite of the fact that fluidized systems are usually used as reactors, the literature on reaction kinetics in fluid beds is scarce. The object of this work was to determine the effect on reaction kinetics of changes in a fluidized bed used as a reactor. Insofar as possible, the purely chemical effects were separated from the physical effects of fluidization. The ideal result of the work would be the development of information by which laboratory studies could be used to predict reaction rates in large fluidized reactors.

Previous Work

The low temperature catalytic oxidation of ammonia, which was used for the kinetic studies, has been described by Bodenstein (1) and Zawadzki (13). The formation of nitrous oxide and nitrogen in the presence of metal oxide catalysts consists of surface catalyzed reactions which may be used as a measure of gas-solid contact. Other authors (6) (7) have described ammonia oxidation over oxides of manganese and bismuth near 250° C.

In general, the interpretation of fluidized reaction data cannot be patterned after kinetics in fixed bed reactors. Several authors (2) (10) (11) have noted a high degree of heterogeneity in a gas-fluidized bed. Gilliland and Mason (3) (4) have described the mixing and by-passing associated with fluidization. Because of the heterogeneous nature of the system, treatment of reaction data probably can be handled best by reference to some characteristic properties of fluidized beds.

Toomey and Johnstone (12) have suggested a two-phase theory of fluidization which postulates a uniform dense suspension of solids in a supporting gas stream (the continuous phase), and a pure gas phase passing through the system as bubbles, slugs, or channels (the discontinuous phase). The two phases are further defined by assuming that the flow rate of the discontinuous phase, V_d, is equal to $(V - V_c)$, where V is the volumetric gas rate, and V_c is the gas rate at incipient two-phase fluidization. By considering the equations for energy transformations in the bed, Toomey derived the expression

$$\log (V/V_c) = (KD_p^{0.5}\text{-}k)\ \Delta P_{KE}/\ \Delta P_{mf}, \qquad (1)$$

where D_p is the particle diameter; ΔP_{KE} is the additional pressure loss above ΔP_{mf}, the pressure loss at incipient fluidization; and K and k are constants. Since ΔP_{KE} is explained as the pressure loss because of kinetic energy transfer from the discontinuous phase to the particles, an equation of similar form may represent reaction rate data as a measure of solid-gas contact.

Experimental

The fluidized reactor used was a 4.5 inch i.d. stainless steel column, 43 inches long. The gas was distributed by a stainless steel porous plate. The temperature of the bed was controlled by a Wheelco controller with a thermocouple placed in a well along the axis of the column.

Measurements were made of the rate of disappearance of ammonia from an ammonia-oxygen gas stream in the presence of a manganese-bismuth oxide catalyst supported on alumina beads. Samples of gas were taken from the inlet and outlet lines and were analyzed for ammonia and water by adsorption on magnesium perchlorate and subsequent titration of the solid. Occasional analyses of some samples of the outlet gas for oxygen, nitrous oxide, and nitrogen were made in an Orsat-type unit (9).

Results And Conclusions

Nine series of runs were made in which four sizes of catalyst particles, three initial bed depths, three feed concentrations, and two temperatures were used. Each series consisted of measurements of the reaction rates at several flow rates ranging from a value near minimum fluidization to one four or five times as large. The fractional incremental increase in reaction rate above that at incipient two-phase fluidization was found to be proportional to the logarithm of the flow rate. An equation of the same form as Equation 1 was found to fit all the data except those for the highest (20%) ammonia concentration. This equation is

$$R_d/R_c = K \log (V/V_c), \qquad (2)$$

where R is the rate of reaction, V is the volumetric rate of gas flow, the subscript $_c$ refers to the rate at incipient two-phase fluidization, and R_d is equal to $(R - R_c)$. K is a constant for a given bed, but increases with increasing initial bed depth, and decreases with increasing particle size.

The two-phase fluidization theory infers that most of the solid resides in the continuous phase. Therefore, it may be assumed that for a catalytic reaction, all of the reaction occurs in the continuous phase, and that before a gas component in the discontinuous phase may react, it must be physically transferred into the continuous phase. Based on this reasoning, mathematical analyses for two limiting cases of mixing within the continuous phase have been made. For the case of no longitudinal mixing of the continuous phase, the relation between the extent of reaction and two constants k_d and k_c is analytical. The constant k_d is for the first order process of mass transfer between the phases, and k_c is the reaction rate constant for the continuous phase. For the case of complete mixing within the continuous phase, the extent of reaction may be calculated stepwise using several equations involving the two constants k_d and k_c. The detention time of the gas in each phase was calculated using the equations of Toomey and of Lewis, Gilliland, and Bauer (8). Unfortunately, the

data obtained did not allow an evaluation of these analyses. More kinetic data, particularly to establish specifically the order of the reaction and the value of k_c at incipient two-phase fluidization, are needed to determine the usefulnesss of this concept.

Kivnick and Hixson (5) found that the velocity dependence of the rate of reduction of nickel oxide in a fluid bed could be expressed as

$$U = a\ (v_L)^b, \tag{3}$$

where U is an overall reaction coefficient in lb. moles/ hr., lb., atm.; v_L is the superficial gas velocity; and a and b are constants. The data obtained for the oxidation of ammonia can be represented by an equation of this form for most of the catalyst beds. This empirical correlation does not depend upon the two-phase concept of fluidization, but it is not incompatible with it.

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VITA

James DeHaven Batchelor was born on May 21, 1925, in Winter Park, Florida. After graduation from Winter Park High School in 1942, he entered the University of Virginia. He served in the Army of the United States from 1944 to 1946. After discharge he returned to the University of Virginia and received the Degree of Bachelor of Chemical Engineering in 1948. He entered the Graduate College of the University of Illinois in 1948 and received a Master of Science Degree in 1950. He held a teaching assistantship in Chemical Engineering in the academic years 1948-49 and 1950-51, the Pittsburgh Consolidation Coal Company Fellowship in 1949-50, and the Du Pont Company Fellowship in 1951-52. He is a member of the Raven Society, Tau Beta Pi, Sigma Xi, and Theta Tau.